Nano-Thermal Analysis

Application to Studies of Polymer Blends

In the last decennia there has been a substantial and growing interest in polymer ‘thin' films. These films (typically below 200 nm thickness) show remarkable properties, sometimes completely different from those in bulk. Understanding how the morphology of thin polymer (blend) films evolves with time or preparation methods is of great technological importance [1].

Nano-thermal Analysis

AFM turns out to be the suited technique for studying these films. It is possible to determine different images (e.g. topographic, friction and phase) in one scan. The Anasys Instruments Nano-thermal analyser (nano-TA) add-on used in this work combines the normal AFM modes with spatially resolved thermal analysis. Using a silicon thermal probe, nanometer lateral resolution can be obtained for the thermal analysis, in contrast to the micrometer resolution of the Wollaston thermal probe used in micro-TA [2]. The recorded thermal analysis signal allows one to determine the transition temperature (melting, glass transition temperature) on selected spots of the sample, -aiding in the identification and characterization of the phases.

Some Practical Examples

1. Semi crystalline blends

In the case of isotactic PP/syndiotactic Polypropylene (iPP/sPP) blends an Upper Critical Solution Temperature (UCST) type phase behavior is predicted with -liquid-liquid phase separation occurring prior to crystallization in high molar mass blends [3-4]. Figure 1a shows a 25/75 iPP/sPP blend with a fibrillar semi-crystalline morphology. The identification of the phase-separated morphology by traditional methods such as Optical Microscopy or TEM is not possible due to a lack of contrast [5]. Using nano-TA, the phases can be identified and characterized by exploiting the difference in melting temperature (135 °C for bulk sPP and 165 °C for bulk iPP).

The transition temperatures were measured inside and in the vicinity of the fibrils. The holes resulting from the thermal analysis are displayed in figure 1b and 1c. The data in figure 2 show the deflection of the probe and are the result of the average of
First, the thermal expansion of the probe is monitored, followed by the penetration of the AFM tip into the polymer. The transition temperature is taken as the temperature at which the probe starts sinking into the material.

2. Amorphous blends
Poly(vinylmethylether)/polystyrene (PVME/PS) blends show a Lower Critical Solution Temperature behavior (LCST). This means that, starting from a homogeneous system, they phase-separate when heated above a certain temperature. In thin coatings, the influence of the air-polymer and substrate-polymer interfaces increases with decreasing film thickness and affects the phase-separation behavior and the final morphology [1-6]. This film thickness effect on the phase separation temperature is observed for films with a thickness below 1 μm and is substrate dependent [7]. Thin films were studied on two different substrate chemistries, the natural oxide layer and an HF etched silicon surface.

AFM experiments were carried out at 30 °C in contact mode, acquiring both topographic and lateral force images. At this temperature, the PS rich phase is in the glassy state, which preserves the morphology formed at a more elevated temperature [8].

After annealing above the LCST, a PVME rich phase and a PS rich phase are formed. Figure 3 illustrates the importance of the surface chemistry on the morphology.

Due to its higher surface tension, the PS rich phase forms bumps and the PVME rich phase forms holes. Since holes are associated with higher values of the lateral force, thus with a more viscous material they probably correspond with the PVME rich phase. These indirect findings were confirmed by direct measurements of the glass transition temperature of the different domains with -
nano-TA (fig. 4). Because of the low glass transition temperature and the hydrophilic nature of PVME, nano-TA measurements were performed at -30 °C under N₂ atmosphere.

It is worth noting that PVME is the dispersed phase, although it is the majority component, while in contrast, the PS rich minority phase is acting as a framework. Figure 5 illustrates the lateral resolution of the nano-TA system. The mean hole radius of the seven holes equals 100 nm. The size of the holes depends on the penetration depth and on the shape of the AFM tip.

**Conclusion**

Nano-thermal analysis in combination with AFM proves to be a very valuable tool for the study of polymeric coatings and surfaces in general, since it allows not only imaging but also direct identification and characterization of the different domains at the sample surface on a 100 nm scale.

**Acknowledgement**

The Fund for Scientific Research Flanders (FWO-Vlaanderen) is kindly acknowledged for financing this research.

**References:**


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